



DECLARATION

I, the undersigned, of 101, 4-5, Uenomaru 2-chome, Akashi-shi, Hyogo, Japan, hereby certify that I am well acquainted with the English and Japanese languages, that I am an experienced translator for patent matter, and that the attached document is a true English translation of

Japanese Patent Application No. **11-257186**

that was filed in Japanese.

I declare that all statements made herein of my own knowledge are true, that all statements on information and belief are believed to be true, and that these statements were made with the knowledge that willful statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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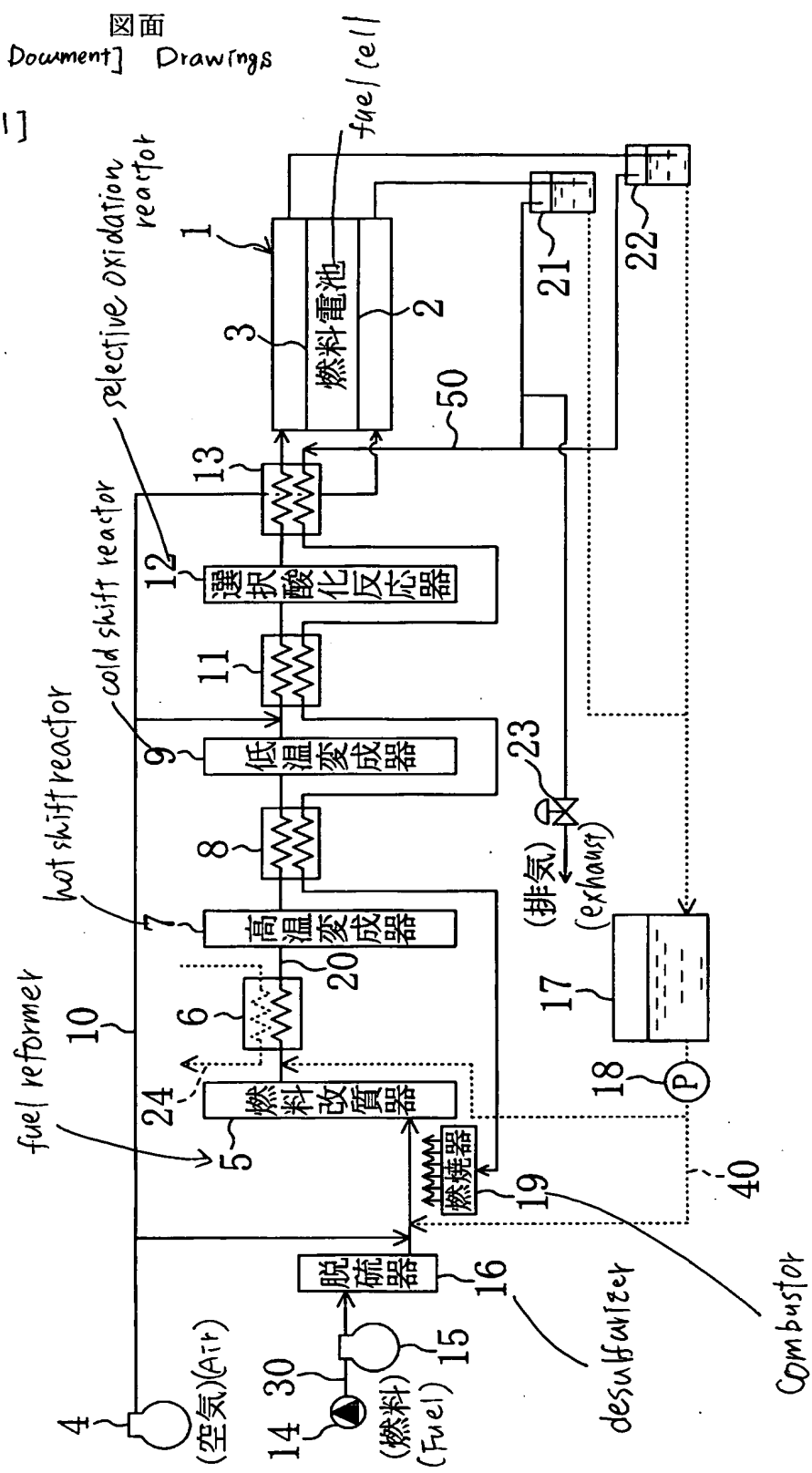
A handwritten signature in black ink, appearing to read "Chie Okamoto".

Chie Okamoto

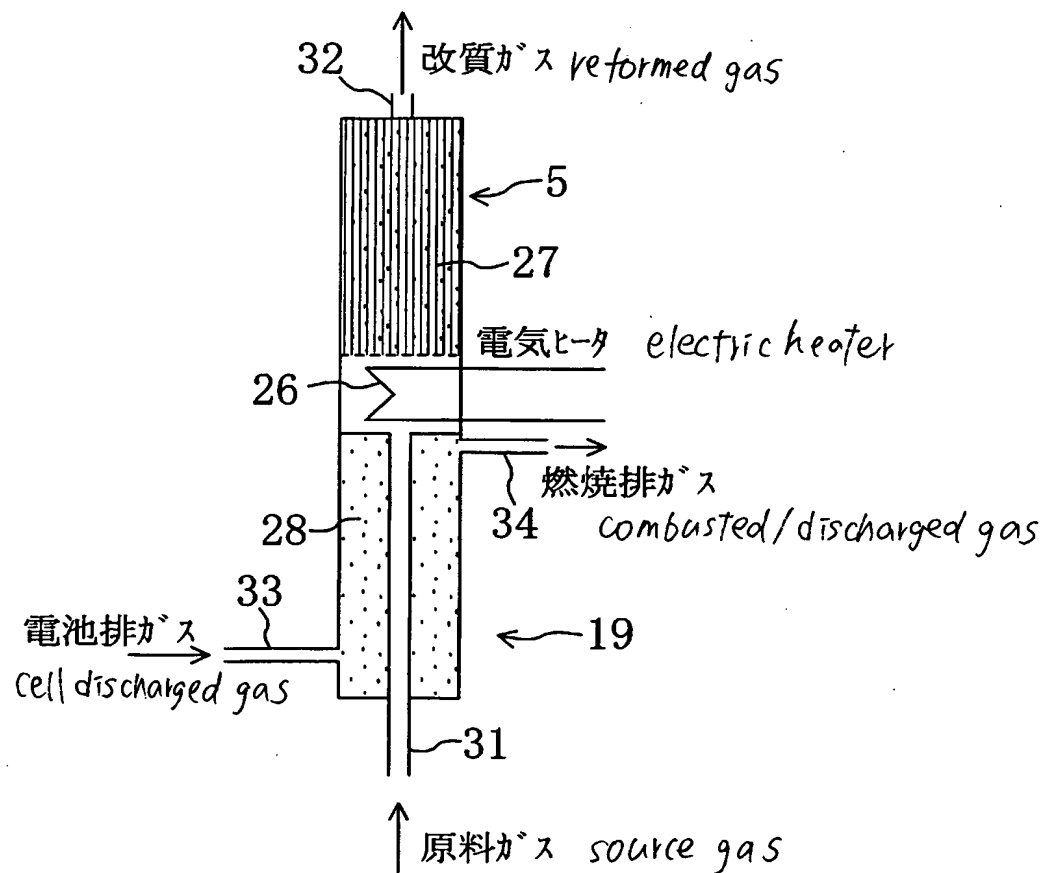
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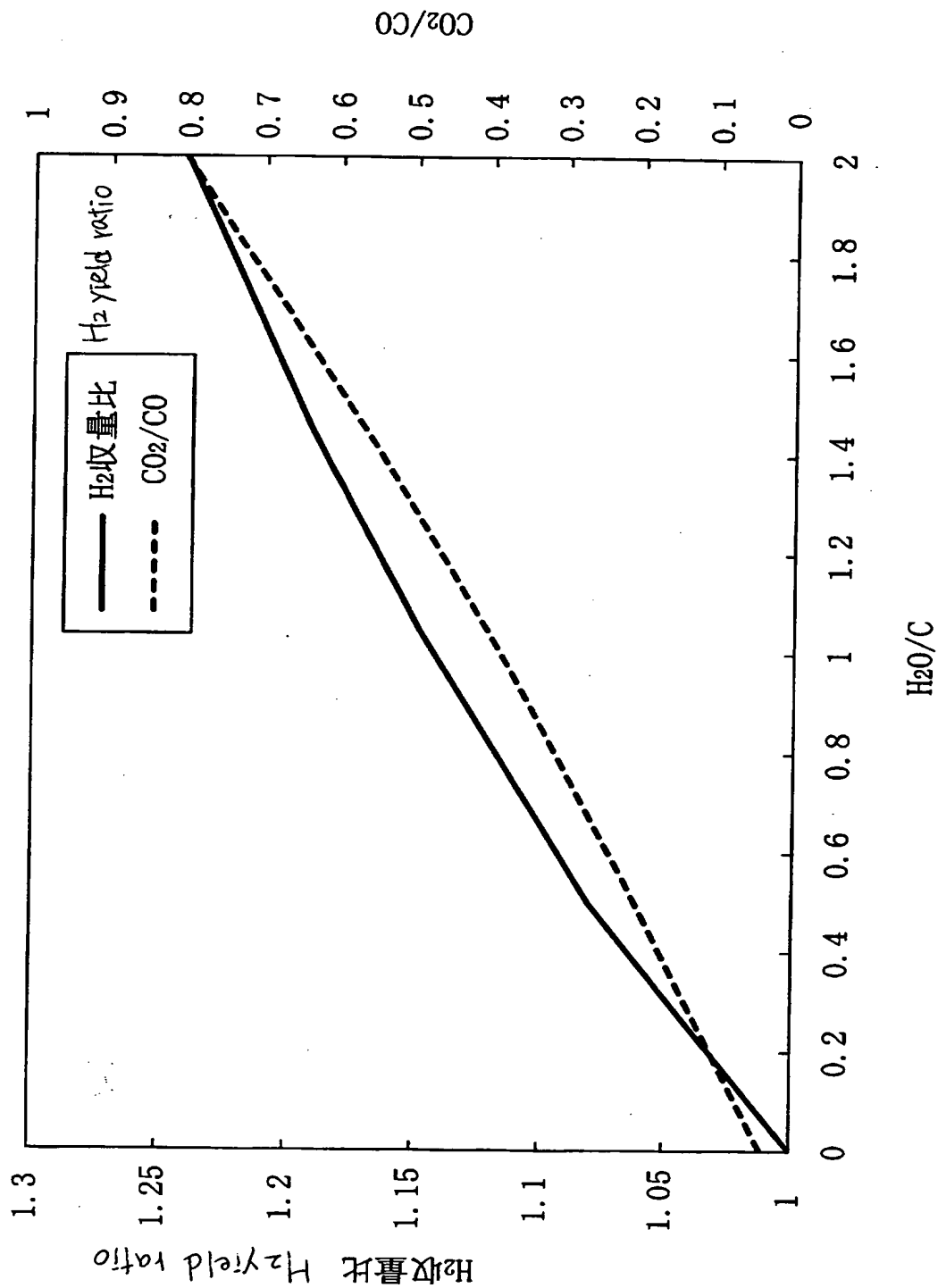
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【Name of Document】 Drawings
【図1】
【Figure 1】



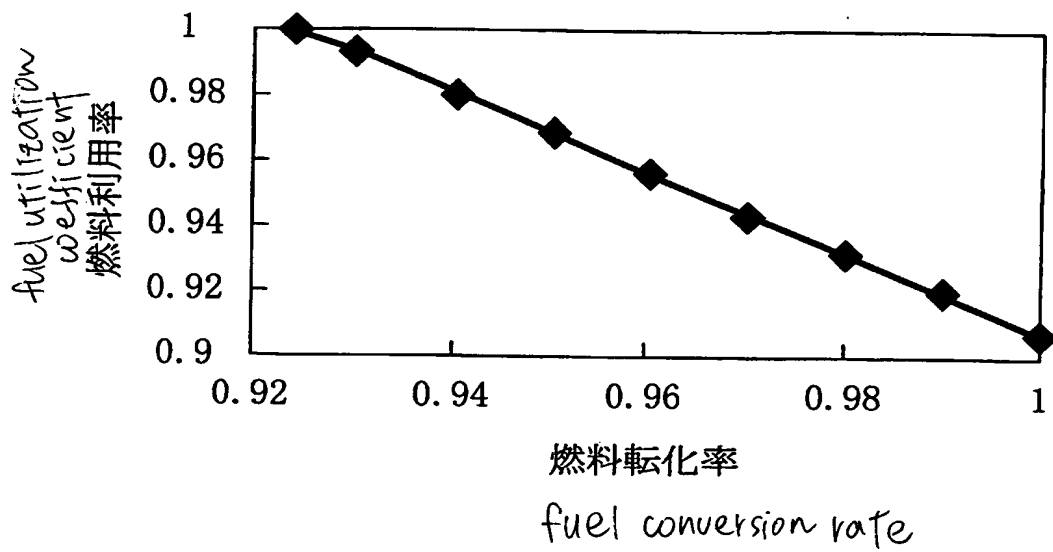
【図2】
[Figure 2]



【図3】
[Figure 3]



【図5】
[Figure 5]



[Name of the Document] Specification

[Title of the Invention] Fuel Cell System

[Claims]

[Claim 1] A fuel cell system which comprises a fuel reformer (5) for reforming a
5 source fuel of the hydrocarbon family to generate hydrogen and which also includes a fuel
cell (1) for generating electricity by using, as a fuel, hydrogen produced by the fuel
reformer (5), said fuel cell system characterized in that

said fuel reformer (5) is provided with a catalyst (27) which exhibits an activity to a
partial oxidation reaction of said source fuel, and

10 steam supply means (35, 40) is provided for supplying steam to said fuel reformer
(5) to cause, in said fuel reformer (5), a water gas shift reaction in which CO produced in
said partial oxidation reaction is a reactant.

[Claim 2] The fuel cell system of claim 1, characterized in that said water gas shift
reaction is controlled such that the CO_2/CO ratio, which is the ratio of CO_2 to CO in an
15 outlet gas of said fuel reformer (5), is not less than 0.2.

[Claim 3] The fuel cell system of claim 1 or 2, characterized in that the rate at
which said source fuel and said steam are supplied to said fuel reformer (5) is set in such a
manner that the $\text{H}_2\text{O}/\text{C}$ ratio, which is the ratio of the number of moles of said steam to the
number of moles of carbon of said source fuel, is not less than 0.5.

20 [Claim 4] The fuel cell system of claim 3, characterized in that said $\text{H}_2\text{O}/\text{C}$ ratio is
not more than 3.

[Claim 5] The fuel cell system of any one of claims 1 through 4, characterized in
that the outlet gas temperature of said fuel reformer (5) is not more than 800 degrees
centigrade.

[Claim 6] The fuel cell system of any one of claims 1 through 5, characterized in that the rate at which said source fuel and oxygen are supplied to said fuel reformer (5) is set in such a manner that the O_2/C ratio, which is the ratio of the number of moles of said oxygen to the number of moles of carbon of said source fuel, is not less than 0.9 time the O_2/C theoretical mixture ratio in said partial oxidation reaction.

[Claim 7] The fuel cell system of any one of claims 1 through 5, characterized in that the rate at which said source fuel and oxygen are supplied to said fuel reformer (5) is set in such a manner that the O_2/C ratio, which is the ratio of the number of moles of said oxygen to the number of moles of carbon of said source fuel, is greater than the O_2/C theoretical mixture ratio in said partial oxidation reaction.

[Claim 8] The fuel cell system of claim 6 or 7, characterized in that said O_2/C ratio is not more than 1.5 times said O_2/C theoretical mixture ratio.

[Claim 9] The fuel cell system of any one of claims 1 through 8, characterized in that an active site of said catalyst (27) is formed of at least one of rhodium and ruthenium.

[Claim 10] The fuel cell system of claim 9, characterized in that said catalyst (27) is supported on a honeycomb monolith carrier.

[Claim 11] The fuel cell system of any one of claims 1 through 10, characterized by further comprising

discharged gas supply means (35), as said steam supply means, for supplying a gas discharged from an oxygen electrode of said fuel cell to said fuel reformer (5).

[Claim 12] The fuel cell system of claim 11, characterized by further comprising output current control means (38) for controlling an output current of said fuel cell so that the oxygen concentration and the steam concentration of the discharged gas that is supplied to said fuel reformer (5) fall within their respective given ranges.

[Claim 13] The fuel cell system of claim 11, characterized by further comprising

output current control means for controlling an output current of said fuel cell so that the coefficient of utilization of oxygen of said fuel cell ranges from 0.4 to 0.75.

[Claim 14] The fuel cell system of claim 11, characterized by further comprising air supply means (39) for supplying air to said fuel reformer (5).

5 [Detailed Description of the Invention]

[Technical Field to which the Invention Belongs]

The present invention relates to a fuel cell system.

[Prior Art]

Fuel cells are generally known as an electricity generator in which hydrogen
10 delivered as a fuel to the negative electrode and oxygen delivered as an oxidant to the positive electrode react together through an electrolyte. The hydrogen used for the fuel cell can be generated by reforming hydrocarbon or methanol.

Japanese Patent Gazette No. S58-57361 shows a technique in which either air, air/oxygen, or air/steam is acted on hydrocarbon in the presence of a rhodium catalyst for
15 obtaining hydrogen and CO (carbon monoxide) by partial oxidation. The reaction temperature is from 690 to 900 degrees centigrade. The air and oxygen are used as an oxidant for the hydrocarbon and the steam is used to generate, by steam reforming reaction, hydrogen from a fuel which has been left unoxidized in the oxidation reaction. Accordingly, reactions taking place on a rhodium catalyst when air and steam are acted on
20 hydrocarbon are a partial oxidation reaction and a steam reforming reaction.

Japanese Patent Gazette No. S54-76602 shows a technique in which a free-oxygen-containing gas is acted on hydrocarbon at a temperature in the range of 815 to 1930 degrees centigrade and under an absolute atmospheric pressure in the range of 1 to 250 ata for generating hydrogen and CO by partial oxidation and, in addition, steam is added for
25 the preheating, dispersion, and transfer of a temperature moderator and hydrocarbon fuel.

Japanese Patent Gazette No. H06-92603 shows a technique in which hydrocarbon, oxygen-containing gas, and steam are subjected, under a pressure in the range of 2 to 100 bars and at a temperature in the range of 750 to 1200 degrees centigrade (preferably, in the range of 1000 to 1200 degrees centigrade), to a partial oxidation reaction in the presence of
5 a catalyst for generating hydrogen and CO.

Japanese Patent Gazette No. H07-57756 shows a hydrogen gas generator having a fuel reformer in which steam is acted on hydrocarbon in the presence of a catalyst for generating hydrogen and CO by steam reforming reaction. Oxygen is introduced into the fuel reformer to cause, at the same time, a partial oxidation reaction of the hydrocarbon to
10 take place. Since the steam reformation reaction is endothermic, this compensates for the heat necessary for the steam reformation reaction by making utilization of the partial oxidation reaction which is exothermic.

Japanese Patent Gazette No. H10-308230 shows a fuel cell electricity generation apparatus comprising a fuel reformer for reforming hydrocarbon into hydrogen by partial
15 oxidation reaction in the presence of a catalyst, a CO shift reactor for causing CO produced in the reforming process to undergo oxidation by a water gas shift reaction, and a selective oxidization device for subjecting the remaining CO to selective oxidization. This prior art further shows that in addition to the catalyst exhibiting an activity to the partial oxidation reaction, the fuel reformer is filled with another catalyst exhibiting an activity to a steam
20 reforming reaction of the hydrocarbon. Hydrocarbon, oxygen, and steam are supplied to the reformer to produce hydrogen by the partial oxidation reaction of the hydrocarbon and the steam reforming reaction.

[Problems that the Invention is to solve]

As described above, when performing the reforming of hydrocarbon into hydrogen
25 by partial oxidation reaction, it has been known that oxygen and steam are acted on the

hydrocarbon in the presence of a catalyst. The steam is added for obtaining a steam reforming reaction which is endothermic or for controlling the temperature or the like. This requires that an external heating means with a large heat transfer area be provided in the fuel reformer in order to maintain the reforming reaction. Also, in order to prevent the catalyst electrode of a fuel cell from undergoing poisoning by CO generated by the partial oxidation reaction of the hydrocarbon and the steam reforming reaction, a large-size shift reactor is required for the oxidation removal of CO.

As stated in the foregoing patent gazettes (H07-57756 and H10-308230), with a view to eliminating the need for an external heating means, there is a concept that an absorption of heat by the steam reforming reaction is compensated for by a liberation of heat by the partial oxidation reaction. However, for the case of methane, the heat of reaction of the steam reforming reaction is about 205 kJ/mol (heat absorption), whereas the heat of reaction of the partial oxidation reaction is only about 36 kJ/mol, and the difference in heat quantity is large. Accordingly, it is practically difficult to eliminate the need for an external heating means by just employing the concept that steam is added for the purpose of mainly causing a steam reforming reaction to take place.

Accordingly, an object of the present invention is to reduce the external heat quantity required for maintaining the fuel reforming reaction and to further reduce it to zero.

Furthermore, another object of the present invention is to reduce the amount of CO that is produced by the reforming of fuel and thereby to reduce the load of a CO shift reactor.

Further, still another object of the present invention is to accomplish effective utilization of heat in the entire fuel cell system and to provide a simplified system configuration.

[Means for Solving the Problems]

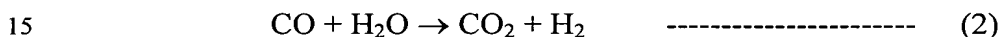
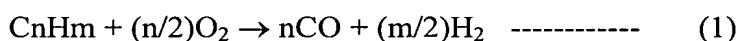
In order to accomplish these objects, in the present invention, partial oxidation and water gas shift reactions are proceeded successively.

The present invention provides a fuel cell system which includes a fuel reformer (5) for reforming a source fuel of the hydrocarbon family to generate hydrogen and which also includes a fuel cell (1) for generating electricity by using, as a fuel, hydrogen produced by the fuel reformer (5), and which is characterized in that

said fuel reformer (5) is provided with a catalyst (27) which exhibits an activity to a partial oxidation reaction of said source fuel, and

steam supply means (35, 40) is provided for supplying steam to said fuel reformer (5) to cause, in said fuel reformer (5), a water gas shift reaction in which CO produced in said partial oxidation reaction is a reactant.

The above successive reactions are expressed as follows.



The reaction equation (1) is for the partial oxidation reaction. Target hydrogen can be obtained by this reaction, and CO that is produced simultaneously with the hydrogen is oxidized by the water gas shift reaction expressed by the reaction equation (2) and hydrogen is also generated during the water gas shift reaction. The addition of steam to the source gas does not much affect the fuel conversion rate in the partial oxidation reaction of the reaction equation (1), but the steam addition makes it easy for the water gas shift reaction of the reaction equation (2) to take place (because the equilibrium inclines toward the generation side), thereby increasing the yield of hydrogen.

The partial oxidation reaction of the reaction equation (1) is an exothermic reaction, and when the source fuel C_nH_m is methane (CH_4), $\Delta H = -36.07 \text{ kJ/mol}$. The water gas

shift reaction of the reaction equation (2) is also an exothermic reaction, and $\Delta H = -41.12$ kJ/mol. Accordingly, either the fuel reformer (5) or the source gas (source fuel, oxygen or air, and steam) must be heated up to a certain temperature in order to initiate a reforming reaction. However, once the reaction starts, an amount of heat necessary for maintaining the reaction can be obtained from the reaction heat. This reduces the amount of external heating, therefore making it possible to eliminate the need for external heating.

Further, since the CO produced in the partial oxidation reaction of the reaction equation (1) is oxidized by the water gas shift reaction of the reaction equation (2), this reduces the CO concentration of the reformed gas supplied to the fuel cell from the fuel reformer (5). Accordingly, when a CO shift reactor (which oxidizes CO by the water gas shift reaction) and a CO selective oxidation reactor are provided, their loads are reduced and thus their sizes are also reduced.

If the water gas shift reaction is controlled such that the CO_2/CO ratio, which is the ratio of CO_2 to CO in an outlet gas of the fuel reformer (5), is not less than 0.2, an increased hydrogen yield can be achieved and the CO shift reactor can has its loads reduced in the following step.

The above point will be made clearer in the description of the following embodiments of the present invention. The fact that the CO_2/CO ratio is high means that the water gas shift reaction is proceeding, whereby hydrogen is produced.

The increase in the CO_2/CO ratio, i.e., the proceeding of the water gas shift reaction, relates to the rate at which the source fuel and steam are supplied to the fuel reformer (5), and it is therefore preferable that the $\text{H}_2\text{O}/\text{C}$ ratio, which is the ratio of the number of moles of the steam to the number of moles of carbon of the source fuel, is not less than 0.5.

In the present invention, the addition of steam is for the water gas shift reaction, and if the $\text{H}_2\text{O} / \text{C}$ ratio increases, this causes the water gas shift reaction to efficiently

proceed. If the ratio is less than 0.5, then the water gas shift reaction will not be proceeded sufficiently. As a result, the CO concentration of a gas obtained increases and the downsizing of the CO shift reactor cannot be achieved. Furthermore, the hydrogen yield is not improved.

5 Further, by setting the H_2O/C ratio to 0.5 or more, the CO concentration of the reformed gas is positively reduced by the water gas shift reaction. Thus, the temperature of the CO shift reactor can be prevented from becoming excessively high. In other words, when the concentration of CO in the reformed gas is high, the CO shift reactor undergoes an excessive increase in its temperature by the water gas shift reaction there (for example,
10 the shift reactor temperature becomes higher than the shift reactor inlet gas temperature by 100 K or more). This may result in catalyst sintering or early-stage degradation. However, such is prevented.

It is preferable that the H_2O/C ratio be not more than 3. Increasing the H_2O/C ratio, i.e., increasing the amount of steam, provides the advantage that the water gas shift
15 reaction is promoted. However, an increase in the steam amount requires a large amount of heat corresponding to that increase, therefore resulting in the drop in energy efficiency. Accordingly, the H_2O/C ratio is set to 3 or less.

It is preferable that the outlet gas temperature of the fuel reformer (5) be not more than 800 degrees centigrade. As stated above, both the partial oxidation reaction and the
20 water gas shift reaction are an exothermic reaction. Therefore, unlike the steam reforming reaction which is an endothermic reaction, if the reaction temperature becomes excessively high, this provides disadvantages in the reaction proceeding. It is therefore preferable that the lower limit of the outlet gas temperature be about 450 degrees centigrade. The reason is that if the outlet gas temperature falls below such a lower limit, this makes the partial
25 oxidation reaction and the water gas shift reaction difficult to proceed.

It is preferable that the rate at which the source fuel and oxygen are supplied to the fuel reformer (5) is set such that the O_2/C ratio, which is the ratio of the number of moles of the oxygen to the number of moles of carbon of the source fuel, is not less than 0.9 time the O_2/C theoretical mixture ratio in the partial oxidation reaction.

5 As can be seen obviously from the reaction formula (1), the O_2/C theoretical mixture ratio in the partial oxidation reaction is 0.5. Therefore, the O_2/C ratio is not less than 0.45. Then, even when the flow rate (space velocity) of the source gas that is supplied to the fuel reformer (5) is high, it is possible to provide a high fuel conversion rate (reforming rate).

10 If the lower limit of the ratio is set to fall below the theoretical mixture ratio, there is the possibility that a part of the source fuel undergoes a steam reforming reaction. However, the percentage thereof is slight, and thus that the thermal effect (the temperature drop) on the main reaction (the partial oxidation reaction) is negligible.

Suppressing the occurrence of such a steam reforming reaction as much as possible
15 can be achieved by making the O_2/C ratio greater than the theoretical mixture ratio, i.e., 0.5. However, if the O_2/C ratio is increased excessively, the complete oxidation reaction is likely to occur, leading to the drop in the yield of hydrogen. Therefore, the upper limit of the O_2/C ratio is preferably 1.5 times the O_2/C theoretical mixture ratio, i.e., about 0.75.

As the source fuel of the hydrocarbon family, it is possible to employ propane,
20 natural gas (including LNG), naphtha, kerosene, liquefied petroleum gas (LPG), and city gas, in addition to methane.

As a catalyst metal of the catalyst (27) exhibiting an activity to the partial oxidation reaction, rhodium and ruthenium are preferable. These catalyst metals may be supported on a carrier (support) in the form of a metal simple substance, in the form of an alloy, or in
25 the form of a compound (for example, an oxide). Further, catalyst metals of two or more

kinds (for example, rhodium and ruthenium) may be supported on the same carrier. Alternatively, a mixture of catalyst metals of two or more kinds supported on respective carriers may be applicable.

As the carrier, inorganic porous materials whose specific surface area is large are preferable, such as an alumina.

The fuel reformer (5) can be filled with the catalyst (27) of the carrier carrying thereon a catalyst metal, in the form of a pellet, or the catalyst (27) may be supported on a monolith carrier by a binder (for example, a honeycomb monolith carrier).

Although the oxygen (or air) and steam of the source gas can be supplied to the fuel reformer (5) from respectively-provided supply sources, the discharged gas of the fuel cell can be utilized instead of using them. That is, a gas expelled from the oxygen electrode of the fuel cell contains therein oxygen that has not been used in the cell reaction and steam produced in the cell reaction. Therefore, if a discharged gas supply means for supplying the discharged gas of the oxygen electrode to the fuel reformer (5) is provided, it is then possible to omit the provision of the oxygen (or air) supply source, steam supply source, and their supply piping. This achieves a simplified fuel cell system configuration. However, a means for a supply of oxygen (or air) and a means for steam supply may be provided separately for supplying oxygen and steam to the discharged gas of the oxygen electrode.

Further, if an output current control means capable of controlling the output current of the fuel cell is provided, this makes it possible to control the oxygen concentration and the steam concentration of a discharged gas that is supplied to the fuel reformer (5) to fall within their respective given ranges.

That is, the coefficient of fuel (hydrogen) utilization and the coefficient of oxygen (air) utilization in the fuel cell vary with the load (the amount of electric power used) of the

fuel cell. In other words, where the amount of fuel flowing into the fuel cell and the amount of oxygen flowing into the fuel cell are fixed, if the output current value of the cell is varied, the amount of hydrogen and oxygen that is consumed in the cell reaction varies. This is accompanied with a change in the amount of steam produced. Accordingly, by
5 controlling the output current value, it becomes possible to supply to the fuel reformer (5) a discharged gas with a given oxygen concentration and a given steam concentration that are suitable for the reforming of fuel.

It is preferable that, in the fuel cell, the output current is controlled such that the oxygen utilization coefficient ranges between 0.4 and 0.75 (40-75% of the amount of
10 oxygen supplied). Because of this, it is possible to control the H_2O/C ratio of a source gas for the fuel reformer (5) to range between about 0.67 and about 3.0.

That is, in the fuel cell, the amount of steam produced is theoretically two times the amount of oxygen consumed ($O_2 + 2H_2 \rightarrow 2H_2O$). Thus, if the oxygen utilization coefficient is 0.4, an amount of steam equivalent to twice the oxygen utilization coefficient
15 (i.e., 0.8) is produced, and the residual oxygen amount is an equivalent amount of 0.6. Therefore, the H_2O/O_2 ratio of the discharged gas is (0.8/0.6). If the amount of supply of the discharged gas to the fuel reformer (5) is controlled such that the O_2/C ratio of the source gas is a stoichiometric ratio of 0.5, then the H_2O/C ratio of the source gas is as follows.

20
$$H_2O/C \text{ ratio} = 0.5 \times (0.8/0.6) = \text{about } 0.67$$

Likewise, the following calculation is carried out for the oxygen utilization coefficient = 0.75.

$$H_2O/C \text{ ratio} = 0.5 \times (1.5/0.25) = 3$$

As described above, in the fuel reformer, a reformed gas, whose CO concentration
25 is low, can be obtained. However, in order to further reduce the CO concentration, at least

one of a CO hot shift reactor, a CO cold shift reactor, and a CO partial oxidation reactor may be provided and the reformed gas is passed therethrough and supplied to the fuel cell.

[Effects of the Invention]

As described above, according to this invention, in a fuel cell system including a
5 fuel reformer (5) and a fuel cell, a catalyst (27) which exhibits an activity to a partial
oxidation reaction of a source fuel of the hydrocarbon family is provided, and steam supply
means is also provided for supplying steam to said fuel reformer (5) to cause, in said fuel
reformer (5), a water gas shift reaction in which CO produced in said partial oxidation
reaction is a reactant. Thus, the yield of hydrogen is improved by the partial oxidation
10 reaction and the water gas shift reaction, and it is possible to downsize an external heating
means for maintaining the fuel-reforming reaction or to omit such external heating means.
Furthermore, the CO concentration of a reformed gas is reduced, and devices used in a
subsequent treatment for further reducing the CO concentration can also have their sizes
reduced.

15 Also, if the water gas shift reaction is controlled such that the CO_2/CO ratio in an
outlet gas of the fuel reformer (5) is not less than 0.2, the yield of hydrogen is
advantageously improved. And, if the $\text{H}_2\text{O}/\text{C}$ ratio of the source gas supplied to the fuel
reformer (5) is not less than 0.5, the yield of hydrogen is advantageously improved in the
water gas shift reaction.

20 Moreover, if the temperature of the outlet gas of the fuel reformer (5) is not more
than 800 degrees centigrade, the partial oxidation reaction and the water gas shift reaction
proceed more efficiently.

If the O_2/C ratio of the source gas supplied to the fuel reformer (5) is not less than
0.9 time the O_2/C theoretical mixture ratio in the partial oxidation reaction, a high fuel
25 conversion rate (reforming rate) can be advantageously provided.

In addition, if the upper limit of the H_2O/C ratio is 3.0, energy loss can be reduced. If the O_2/C ratio is 1.5 times the O_2/C theoretical mixture ratio or less, it is possible to advantageously prevent the complete combustion of the source fuel and maintain the fuel-reforming efficiency at a high level.

5 If a catalyst containing rhodium or ruthenium is used as the catalyst (27) of the fuel reformer (5), the partial oxidation reaction can be advantageously proceeded.

If a discharged gas expelled from the oxygen electrode of the fuel cell is supplied to the fuel reformer (5) as the reformed gas, it is then possible to omit the provision of the oxygen (or air) supply source, the steam supply source, and their supply piping. Thus, the
10 fuel cell system configuration can be advantageously simplified. In that case, if an output current control means capable of controlling the output current of the fuel cell is provided, this makes it possible to easily control the oxygen concentration and the steam concentration of a discharged gas that is supplied to the fuel reformer (5) to fall within their respective given ranges.

15 [Embodiments of the Invention]

Hereinafter, embodiments of the present invention will be described with reference to the accompanying drawings.

(Description of entire fuel cell system)

Figure 1 shows a configuration of the fuel cell system of the present invention, in
20 which the reference numeral 1 denotes a fuel cell of a solid polyelectrolyte type having an oxygen electrode (cathode) 2 which is a catalyst electrode and a hydrogen electrode (anode) 3 which is also a catalyst electrode. An air compressor 4 is connected to the oxygen electrode 2 by an air supply pipe 10. A fuel reformer 5 is connected to the hydrogen electrode 3 by a reformed gas supply pipe 20. In the reformed gas supply pipe
25 20 are a first heat exchanger 6, a CO hot shift reactor 7, a second heat exchanger 8, a CO

cold shift reactor **9**, a third heat exchanger **11**, a CO selective oxidation reactor **12**, and a fourth heat exchanger **13** which are disposed in that order in the direction toward the fuel cell **1**.

A source gas supply pipe **30** establishes connection between the fuel reformer **5** and
5 a source fuel supply (city gas) **14**. A gas compressor **15** and a desulfurizer **16** are disposed in the source gas supply pipe **30** in that order in the direction toward the fuel reformer **5**. Moreover, a pipe, branching off from the air supply pipe **10**, is connected to the fuel reformer **5** so that air for a partial oxidation reaction is supplied from the air compressor **4** to the fuel reformer **5**, and the fuel reformer **5** and a water tank **17** are connected together
10 by a supply pipe **40** so that water for obtaining steam for a water gas shift reaction is supplied, in an atomized form, to the fuel reformer **5**. Disposed in the water supply pipe **40** is a pump **18**.

A source fuel, air and steam are heated by the combustor **19** and supplied to the fuel reformer **5** from the source fuel supply **14**, air compressor **4**, and water tank **17**,
15 respectively. Further, connected to a portion of the reformed gas supply pipe **20** located upstream of the first heat exchanger **6** is a pipe which branches off from the water supply pipe **40** for a supply of water in an atomized form to obtain steam for the water gas shift reaction. Connected to a portion of the reformed gas supply pipe **20** located upstream of the third heat exchanger **11** is a pipe which branches off from the air supply pipe **10** for a
20 supply of air for the selective oxidation reactor **12**.

It is arranged such that discharged gases from the oxygen and hydrogen electrodes **2** and **3** of the fuel cell **1** are passed through steam separators **21** and **22**. Thereafter, these gases are merged together and supplied, through a gas pipe **50**, to the combustor **19** as a gas for combustion. The discharged gas of the oxygen electrode **2** can be suitably vented
25 by a valve **23** to atmosphere. The gas pipe **50** is so laid out as to pass through the fourth

heat exchanger 13, through the third heat exchanger 11, and through the second heat exchanger 8 in that order, and the discharged gas is heated by heat exchange with the reformed gas in each heat exchanger and supplied to the combustor 19. Accordingly, the reformed gas is, on the contrary, cooled in each heat exchanger and supplied to the fuel cell

5 1. Another cooled water pipe 24 passes through the first heat exchanger 6 and the reformed gas is cooled by heat exchange with the cooled water flowing through the cooled water pipe 24.

The fuel reformer 5 is filled with a catalyst (which is formed of Al_2O_3 carrying thereon either Ru or Rh) that exhibits an activity to a partial oxidation reaction. The CO

10 hot shift reactor 7 is filled with a catalyst, such as Fe_2O_3 and Cr_2O_3 , that exhibits an activity to a water gas shift reaction at high temperatures (400 degrees centigrade or thereabouts). The CO cold shift reactor 9 is filled with a catalyst, such as CuO and ZnO, that exhibits an activity to a water gas shift reaction at low temperatures (180 degrees centigrade or thereabouts). The CO selective oxidation reactor 12 is filled with a catalyst

15 (which is formed of Al_2O_3 or zeolite carrying thereon Ru or Pt) that exhibits an activity to a selective oxidation reaction. The combustor 19 is filled with a combustion catalyst. Furthermore, the fuel reformer 5 is provided with an electric heater for pre-heating.

Figure 2 shows a reactor 25, which is an integration of the fuel reformer 5 and the combustor 19. In the reactor 25 of Figure 2, an electric heater 26 is incorporated between

20 the upper-side fuel reformer 5 and the lower-side combustion 19. A site of the fuel reformer 5 is filled with a honeycomb catalyst 27 of a honeycomb monolith carrier carrying thereon a catalyst. A site of the combustion 19 is filled with a combustion catalyst 28, and a source gas passage 29 extends from a source gas inlet 31 at the lower end to where the electric heater is disposed, passing through the catalyst-filled site of the

25 combustor 19. Moreover, in Figure 2, the reference numeral 32 denotes a reformed gas

outlet, the reference numeral **33** denotes an inlet of the discharged gas from the fuel cell **1**, and the reference numeral **34** denotes a combusted/discharged gas outlet.

In the above-described fuel cell system, since the temperature of the fuel reformer **5** is low when the system is started, the electric heater is operated until the temperature is increased to such an extent that the catalyst becomes active, for example, about 460 degrees centigrade. After the system is started, the electric heater is turned off, and a source gas (source fuel and a mixed gas of air and steam) is pre-heated only in the combustor **19**. The source gas is controlled such that the H_2O/C ratio ranges between 0.5 to 3 and the O_2/C ratio ranges between 0.45 and 0.75, by controlling the supply amount of source fuel, air, and steam. The outlet gas temperature of the fuel reformer **5** is separately controlled so as not to go beyond 800 degrees centigrade. A most preferable operating condition is as follows. That is, the H_2O/C ratio is 1.0, the O_2/C ratio is from 0.52 to 0.60 (more preferably, 0.56), the outlet gas temperature of the fuel reformer **5** is 720 degrees centigrade, and the CO_2/CO ratio of the outlet gas of the fuel reformer **5** is 0.4.

After desulfurization, the source fuel is heated together with air and atomized water, by the electric heater or the combustor **19** and supplied to the catalyst of the fuel reformer **5**. The atomized water is changed to steam by such heating. A partial oxidation reaction of the source fuel occurs on the catalyst of the fuel reformer **5**, thereby producing hydrogen and CO (see Formula (1)). Since there exists steam in the inside of the fuel reformer **5**, this causes, at the same time, a water gas shift reaction to take place. As a result, hydrogen and carbon dioxide are generated, and the CO concentration is reduced (see Formula (2)).

Leaving the fuel reformer **5**, the reformed gas is cooled down to about 400 degrees centigrade in the first heat exchanger **6** and delivered to the CO hot shift reactor **7** where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the shift reactor **7**. Then, leaving the CO hot shift reactor **7**, the reformed gas is

further cooled down to about 180 degrees centigrade in the second heat exchanger 8 and supplied to the CO cold shift reactor 9 where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the shift reactor 9. Then, leaving the CO cold shift reactor 9, the reformed gas is cooled down to about 140 degrees centigrade in the third heat exchanger 11 and supplied to the CO selective oxidation reactor 12 where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the reactor 12. Leaving the CO selective oxidation reactor 12, the reformed gas is cooled down to about 80 degrees centigrade in the fourth heat exchanger 13 and supplied to the hydrogen electrode 3 of the fuel cell 1.

In the fuel cell 1, a cell reaction of $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$ occurs at the surface of the hydrogen electrode 3 and a cell reaction of $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ occurs at the surface of the oxygen electrode 2. Therefore, a discharged gas from the oxygen electrode 2 contains therein residual air that has not been used in the cell reaction and steam produced by the cell reaction. On the other hand, contained in a discharged gas from the hydrogen electrode 3 are hydrogen that has not been used in the cell reaction, non-reformed source fuel, air, and steam.

The discharged gases of the oxygen and hydrogen electrodes 2 and 3 pass through the steam separators 21 and 22 and are merged together. Thereafter, the discharged gas thus merged is heated by heat exchange in the fourth, third and second heat exchangers 13, 11, and 8 and delivered to the combustor 19. The discharged gas contains hydrogen and oxygen which undergo a reaction by the action of the combustion catalyst in the combustor 19, and the resulting reaction heat becomes a preheating supply for the source gas. On the other hand, the non-reformed source material contained in the discharged gas is burned at the same time to become a preheating supply.

(Relationship between $\text{H}_2\text{O}/\text{C}$ ratio, CO_2/CO ratio, and hydrogen yield ratio)

Referring to Figure 3, there is shown a relationship between the H_2O/C ratio of a source gas that is introduced into the fuel reformer 5 (i.e., the ratio of the number of moles of steam to the number of moles of carbon in the source fuel), the CO_2/CO ratio of a reformed gas from the fuel reformer 5 (i.e., the ratio of CO_2 to CO in a reformer outlet gas), and the hydrogen yield ratio by the fuel reformer 5 (i.e., the ratio in which the hydrogen yield is 1 when H_2O/C ratio = 0.5). The operation conditions of the fuel reformer 5 are as follows. The inlet gas temperature is 460 degrees centigrade. The O_2/C ratio (i.e., the ratio of the number of moles of oxygen to the number of moles of carbon of the source fuel) is 0.56. The gas pressure is 150 kPa.

According to Figure 3, as the H_2/C ratio increases, the CO_2/CO ratio likewise increases. The fact that the CO_2/CO ratio is great means that CO changes to CO_2 in the fuel reformer 5. This change is attributed to the complete oxidation reaction of the source fuel as well as to the water gas shift reaction of CO . It is proved that the addition of steam makes it possible to cause the water gas shift reaction to efficiently proceed in the fuel reformer 5, for it is not conceivable that the increase in the H_2/CO ratio (i.e., the increase in the amount of steam) makes the complete oxidation reaction easy to proceed.

Figure 3 shows that the hydrogen yield increases if the H_2/C ratio is not less than 0.5. In order to obtain the increase in the hydrogen yield, the water gas shift reaction in the fuel reformer 5 is so controlled as to increase the CO_2/CO ratio above 0.2. In other words, the hydrogen yield can be increased by controlling the source gas composition, the reaction temperature or others.

(Effect of the type of the catalyst of the fuel reformer on the reformed gas composition)

Referring to Table 1, there is shown a relationship between the inlet gas composition (the source gas composition) and the outlet gas composition (the reformed gas

composition) of the fuel reformer **5** when fuel reforming was carried out employing different catalysts for use in the fuel reformer **5**. Three types of catalysts, i.e., Ni-Al₂O₃ (formed of Al₂O₃ carrying thereon Ni), Rh-Al₂O₃ (formed of Al₂O₃ carrying thereon Rh), and Ru-Al₂O₃ (formed of Al₂O₃ carrying thereon Ru), were used.

5 **TABLE 1**

CATALYST TYPE	GAS	INLET COMPOSITION	OUTLET COMPOSITION
Ni-Al₂O₃	H ₂	-	0.3071
	N ₂	0.4637	0.4728
	CH ₄	0.2200	0.0549
	CO	-	0.1063
	CO ₂	-	0.0590
	O ₂	0.1233	-
	H ₂ O	0.1931	-
	SV(h ⁻¹)	143000	-
Rh-Al₂O₃	H ₂	-	0.3704
	N ₂	0.4638	0.4301
	CH ₄	0.2199	0.0168
	CO	-	0.1261
	CO ₂	-	0.0566
	O ₂	0.1233	-
	H ₂ O	0.1930	-
	SV(h ⁻¹)	143000	-
Ru-Al₂O₃	H ₂	-	0.3649
	N ₂	0.4638	0.4330
	CH ₄	0.2199	0.0215
	CO	-	0.1211
	CO ₂	-	0.0596
	O ₂	0.1233	-
	H ₂ O	0.1930	-
	SV(h ⁻¹)	143000	-

As can be seen from Table 1, for the case of the Rh-Al₂O₃ catalyst and the Ru-Al₂O₃ catalyst, the rate of conversion of methane into hydrogen is high, whereas for the case of the Ni-Al₂O₃ catalyst the conversion rate is low. From this, it is preferable to
10 employ in the fuel reformer **5** either the Rh-Al₂O₃ catalyst or the Ru-Al₂O₃ catalyst.

(Effect of the H₂O/C ratio on the reformed gas composition in the Rh-Al₂O₃ catalyst)

Table 2 shows a relationship between the inlet gas composition (the source gas composition) and the outlet gas composition (the reformed gas composition) of the fuel reformer 5 when the Rh-Al₂O₃ catalyst was employed in the fuel reformer 5, and fuel reforming was carried out at different H₂O/C ratios.

5 **Table 2**

CATALYST TYPE	GAS	INLET COMPOSITION	OUTLET COMPOSITION
Rh-Al ₂ O ₃	H ₂	-	0.3913
	N ₂	0.4637	0.4161
	CH ₄	0.2199	0.0086
	CO	-	0.1175
	CO ₂	-	0.0665
	O ₂	0.1233	-
	H ₂ O	0.1931	-
	SV(h ⁻¹)	29000	-

	H ₂	0.4121
	N ₂	-	0.4029
	CH ₄	0.3758	0.0073
	CO	0.1781	0.0805
	CO ₂	-	0.0973
	O ₂	-	-
	H ₂ O	0.0999	-
	SV(h ⁻¹)	0.3462	-
		29000	

As can be seen from Table 2, as the H₂O/C ratio increases, the CO₂/CO ratio increases and the hydrogen yield also increases. This agrees with the results shown in Figure 3.

10 (Another embodiment of the fuel cell system)

Figure 4 shows another embodiment of the fuel cell system. The present fuel cell system differs from the first fuel cell system. First, instead of introducing to the fuel reformer 5 air from the air compressor 4 and water from the water tank 17, the discharged gas of the oxygen electrode 2 is supplied through a supply pipe 35 to the fuel reformer 5.

15 Second, another power supply 37 and the fuel cell 1 are connected in parallel to an electric

load **36** and a power controller **38** for controlling the output current value of the fuel cell **1** is disposed. Finally, a flow rate control valve **39** is disposed in a branch pipe extendedly arranged from the air supply pipe **10** toward the source gas supply pipe **30** to form an air supply means.

5 As described above, the discharged gas of the oxygen electrode **2** contains steam and unused air. The discharged gas is therefore used as a gas for reforming a source fuel in the fuel reformer **5** and the power controller **38** is disposed to make the composition of the discharged gas suitable for the fuel reforming. By controlling the output current value of the fuel cell **1** with the power controller **38**, the coefficient of utilization of hydrogen and
10 air of the fuel cell **1** varies and, as a result, the oxygen concentration and the steam concentration of the discharged gas of the oxygen electrode **2** vary. The lack of electric power resulting from such control is supplemented by the power supply **37**.

If the coefficient of utilization of hydrogen is 100% when the amount of hydrogen used in the fuel cell **1** is 1L/min (0 °C and 1 atmospheric pressure), then the output current
15 value A at that time is theoretically as follows.

$$A = 2 nF$$

$$= 143 \text{ (ampere)}$$

(A: C(coulomb)/sec; n: mole/sec; and F: Faraday constant)

Accordingly, if the output current value is decreased below the above theoretical
20 value, then both the hydrogen utilization coefficient (the fuel utilization coefficient) and the air utilization coefficient decrease. In that case, the air utilization coefficient is so controlled to fall in the range, for example, between 0.4 and 0.75.

Further, the lack of air when the air utilization coefficient is increased is supplemented by introducing air from the air compressor **4** by the flow rate control valve
25 **39**.

(Relationship between fuel utilization coefficient and fuel conversion rate)

Figure 5 is a graph showing a relationship between the fuel utilization coefficient of the fuel cell 1 and the fuel conversion rate of the fuel reformer 5 at which the energy efficiency reaches a maximum in a fuel cell system which uses a source fuel which has not been reformed and a hydrogen which has not been used of the source fuel supplied from the source fuel supply 14 for fuel gas preheating.

For example, when the fuel conversion rate is 0.94, the fuel utilization coefficient, at which the energy efficiency reaches a maximum, is 0.98. In this example, 6% of the source fuel that has been remained unreformed and 2% of the hydrogen in the reformed gas that has been remained unused in the cell reaction were utilized for source gas preheating.

In each of the embodiments of the present invention, the combustor 19 is provided, wherein the discharged gas of the fuel cell 1 is utilized for source gas preheating. An arrangement may be made in which the provision of the combustor 19 is omitted and the discharged gas is burned in the catalyst to provide another heat supply. The reason is that since both the partial oxidation reaction and the water gas shift reaction occurring in the fuel reformer 5 are exothermic, the reaction temperature is maintained by the exothermic reaction heat after the fuel reformer 5 is heated up to the reaction temperature by the electric heater at the start.

[Brief Explanation of the Drawings]

[Figure 1]

A diagram showing a configuration of a fuel cell system according to an embodiment of the present invention.

[Figure 2]

A cross sectional view showing structures of a fuel reformer and a combustor of the fuel cell system.

[Figure 3]

A graph showing a relationship between the H_2O/C ratio of a source gas, the CO_2/CO ratio of a reformed gas, and the hydrogen yield ratio.

[Figure 4]

A diagram showing a configuration of a fuel cell system according to another embodiment of the present invention.

[Figure 5] A graph showing a relationship between the fuel utilization coefficient and the fuel conversion rate at which the energy efficiency of the fuel cell system reaches a maximum.

[Explanation of the Reference Characters]

1: FUEL CELL

2: OXYGEN ELECTRODE

15 3: HYDROGEN ELECTRODE

4: AIR COMPRESSOR (AIR SUPPLY)

5: FUEL REFORMER

7: CO HOT SHIFT REACTOR

14: WATER TANK (STEAM SUPPLY)

20 27: CATALYST

35: DISCHARGED GAS SUPPLY PIPE (DISCHARGED GAS SUPPLY MEANS)

38: POWER CONTROLLER (OUTPUT CURRENT CONTROL MEANS)

39: FLOW RATE CONTROL VALVE (AIR SUPPLY MEANS)

25 40: WATER SUPPLY PIPE (STEAM SUPPLY MEANS)

[Name of the Document] Abstract

[Abstract]

[Purpose] To reduce a CO concentration in a reformed gas in a fuel reformer of a fuel cell system and make an external heating means for maintaining a reforming reaction unnecessary.

[Solution] A fuel reformer 5 is provided with a catalyst which exhibits an activity to a partial oxidation reaction of a source fuel and steam is supplied to the reformer 5 so that the partial oxidation reaction and a water gas shift reaction occur in the fuel reformer 5.

[Selected Figure] Figure 1